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Facile Fabrication of Uniform Polyaniline Nanotubes with Tubular Aluminosilicates as Templates

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Abstract The uniform polyaniline (PANI) nanotubes, with inner diameter, outer diameter, and tubular thickness of 40, 60, and 10 nm, respectively, were prepared successfully by using natural tubular aluminosilicates as templates. The halloysite nanotubes were coated with PANI via the in situ chemical oxidation polymerization. Then the templates were etched with HCl/HF solution. The PANI nanotubes were characterized using FTIR, X-ray diffraction, and transmission electron microscopy. The conductivity of the PANI nanotubes was found to be $1.752 \times 10^{-5} (\Omega \cdot \text{cm})^{-1}$.

Keywords Polyaniline nanotube · Fabrication · Halloysite nanotube · Template

Introduction

Conducting polymer nanotubes have recently become the object of numerous investigations because of their great potential in device applications, such as transistors [1], sensors [2], actuators [3], batteries [4], and so on. The conducting polymer nanotubes can be chemically or electrochemically synthesized by the “soft” and “hard” template method. In the first approaches, the micelles or assemblies produced by the salts of the organic acids

(such as naphthalenesulfonic acids [5], camphorsulfonic acid [6], 2-acrylamido-2-methyl-1-propanesulfonic acid [7], sulfoxy-terminated dendrons [8], and polymeric acids [9]) and aniline act as the “soft” templates. The polymerization at template interfaces would give rise to polyaniline (PANI) nanotubes. The inner diameters of the PANI nanotubes by the “soft” templates were difficult to control and sometimes the nanofibers or nanoparticles were by-produced [10, 11].

As for the “hard” template approaches, the suitable rod-like objects were used as templates for the polymerization and growth of polymer films, followed by template dissolution. The templates for making PANI nanotubes include track-etched polycarbonate [12–16], porous alumina [17, 18], manganese oxide nanowires [19], polymer fibers [20], and glass tubes [21]. The most remarkable strongpoint of the “hard” template approaches is that the inner diameters of the PANI nanotubes could be controlled by the sizes of the templates used.

Halloysite (formula: $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, 1:1 layer aluminosilicate), a super-fine clay material, often occurs as an ultramicroscopic hollow tubule with a multi-layer wall in nature. Recently, it was used as adsorbents [22], nanocomposites [23], catalyst supports [24], and nanotemplates or nanoscale reaction vessels instead of carbon nanotubes or boron nitride nanotubes [25].

In the present work, we report a template-based fabrication technique for PANI nanotubes with halloysite nanotubes (HNTs) as template. The HNTs associate the chemical properties of halloysite tubule’s outermost surface with the properties of SiO_2 and properties of the inner cylinder core with Al_2O_3 . So the PANI nanotubes were obtained by etching the template with HCl/HF solution after the PANI layers were coated onto the template via in situ soapless emulsion polymerization.

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Experimental Section

Materials

The HNTs with 50 nm in diameter, 500 nm in length, and with 20 nm hollow inner lumen were obtained from Xuyong County in Sichuan province of China. Aniline (analytical grade reagent, Xi'an Reagent Co., Xi'an, China) was freshly distilled reduced under pressure before use. Concentrated hydrochloric acid (HCl), hydrofluoric acid (HF), and ammonium persulfate (APS) were analytical grade reagents received from Tianjin Chemical Co., Tianjin, China, and used without further purification as received. Distilled water was used throughout.

Polyaniline Nanotubes

The polyaniline coated halloysite nanotubes (PANI/HNTs) hybrids were prepared as reported previously [26]: HNTs (3.00 g), aniline (1.50 mL), and conc. HCl (6.00 mL) were mixed into 450 mL water. The mixtures were irradiated ultrasonically for 30 min. Then 100 mL of the acidic aqueous solution of APS (containing APS 6.80 g and conc. HCl 1.00 mL) was added dropwise into the colloidal mixture within 30 min with magnetic stirring in an ice-water bath. And the mixture was stirred for 12 h with magnetic stirring.

The PANI/HNTs hybrids obtained (1.0 g) were dispersed in 100 mL water containing conc. HCl 10 mL and conc. HF 10 mL with ultrasonic irradiation for 30 min and then immersed overnight. The PANI nanotubes produced were washed with water for several times until neutral and dried under vacuum at 40 °C overnight.

Characterization

The conversion of aniline was calculated from the elemental analysis (EA) of C, N and H, performed on Elementar vario EL instrument. Bruker IFS 66 v/s infrared spectrometer was used for the Fourier transform infrared (FT-IR) spectroscopy analysis in the range of 400–4000 cm^{-1} with the resolution of 4 cm^{-1} . The KBr pellet technique was adopted to prepare the sample for recording the IR spectra. The XRD patterns were recorded in the range of $2\theta = 10\text{--}80^\circ$ by step scanning with a Shimadzu XRD-6000 X-ray diffractometer (Shimadzu Corp., Kyoto, Japan). Nickel-filter Cu K α radiation ($\lambda = 0.15418 \text{ nm}$) was used with a generator voltage of 40 kV and a current of 30 mA. The morphologies of the nanotubes were characterized with a JEM-1200 EX/S

transmission electron microscope (TEM) (JEOL, Tokyo, Japan). The powders were dispersed in water in an ultrasonic bath for 5 min, and then deposited on a copper grid covered with a perforated carbon film. The electrical conductivity of the PANI nanotube was measured using SDY-4 Four-Point Probe Meter (Guangzhou Institute of Semiconductor Materials, Guangzhou, China) at ambient temperature.

Results and Discussion

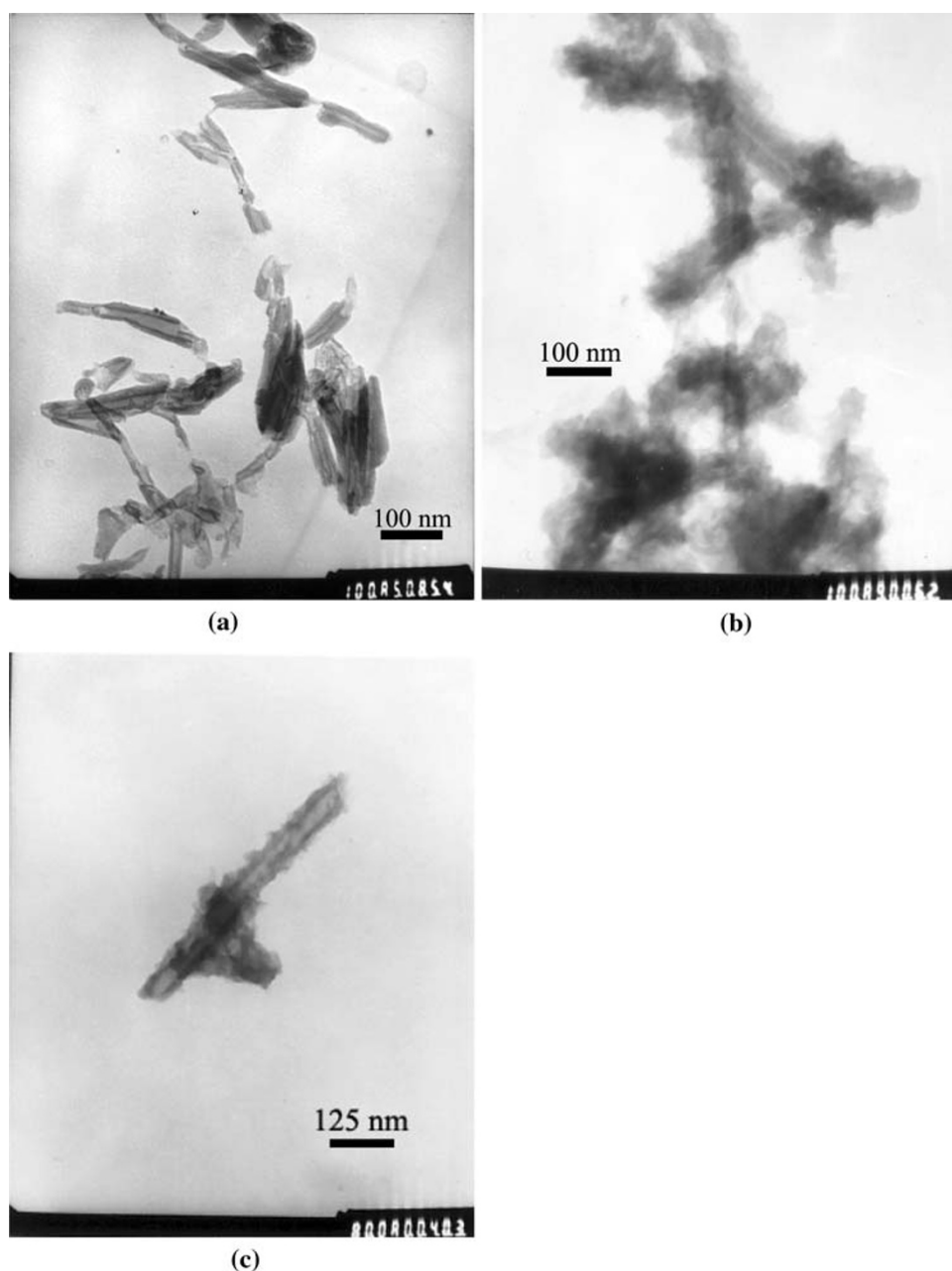
The acidic dopants are generally used in order to form conductive nanostructured PANI (i.e., the emeraldine salt form) by either the “hard” template or the “soft” template methods. As for the HNTs used as the templates in the present work, they might be destroyed in the HCl media because of the Al_2O_3 composition. So the effect of the medium acidities was investigated in the previous work [26]. It was found that 6.00 mL conc. HCl was the maximum amount and the HNTs' structures were destroyed with more conc. HCl added. The weight ratio of the PANI coated with HNTs templates was found to be 43.67%. It indicated that almost all the aniline had been polymerized to form the coaxial coatings on the outer surfaces of HNTs templates.

The TEM image of the PANI/HNTs hybrids is shown in Fig. 1b. It was observed that the diameter of the PANI/HNTs hybrids increased from $\sim 40 \text{ nm}$ of the raw HNTs (Fig. 1a) to about 60 nm. And the inner hollow cavity of the PANI/HNTs hybrids remained at about 10 nm as the raw HNTs (Fig. 1a). It indicated that the polyaniline layer with the thickness of about 10 nm was only coated onto the outer surfaces of the HNTs.

The HNT is a kind of layered aluminosilicate, associated with the chemical properties of halloysite tubule's outermost surface with the properties of SiO_2 and properties of the inner cylinder core with Al_2O_3 . So the HNTs templates could be etched with HCl/HF solution. Furthermore, the two acids cannot dissolve the polyaniline coatings. So the HNTs templates were etched with HCl/HF solution with ultrasonic irradiation for 30 min and then immersed overnight. The PANI nanotubes obtained were analyzed with TEM and the image is shown in Fig. 1c. The PANI nanotube was found to be uniform with inner diameter, outer diameter, and shell thickness of 40, 60, and 10 nm, respectively.

The XRD (Fig. 2) and FTIR (Fig. 3) techniques were used for testifying the complete removal of the HNTs templates. After the etching of the templates with HCl/HF solution, the XRD patterns of the HNTs disappeared

Fig. 1 TEM images: (a) halloysite nanotubes, (b) PANI/HNTs hybrids, and (c) PANI nanotubes



(Fig. 2). It indicated that the crystal structures of the HNTs nanotubes were destroyed. Moreover, in the FTIR spectrum of the PANI nanotubes, only the PANI absorbance remained. All the absorbance peaks (3710 , 3650 , 1640 , 1040 , 910 , 750 , 550 , and 460 cm^{-1}) disappeared. It showed that the HNTs templates were removed completely after the treatment with the mixing acid.

The conductivity of the PANI nanotubes prepared with the present method was found to be $1.752 \times 10^{-5}\text{ }(\Omega\cdot\text{cm})^{-1}$. However, the conductivities of the PANI/SNS nanocomposites were lower than the other popular values

reported. It might be due to the release of the acid dopant during the post-treatments such as washing and drying.

Conclusion

In summary, an efficient approach for the preparation of the uniform PANI nanotubes was achieved. This method included the coating of PANI onto the HNTs templates via the in situ soapless emulsion polymerization and the etching of the HNTs templates with mixing acid. The uniform

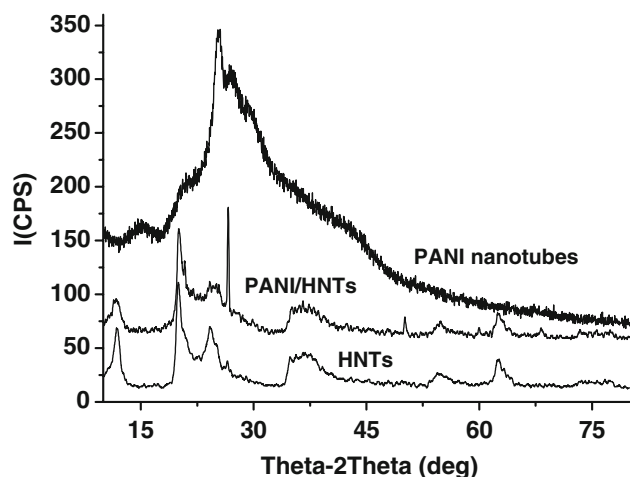


Fig. 2 XRD patterns of raw HNTs, PANI/HNTs hybrids, and PANI nanotubes

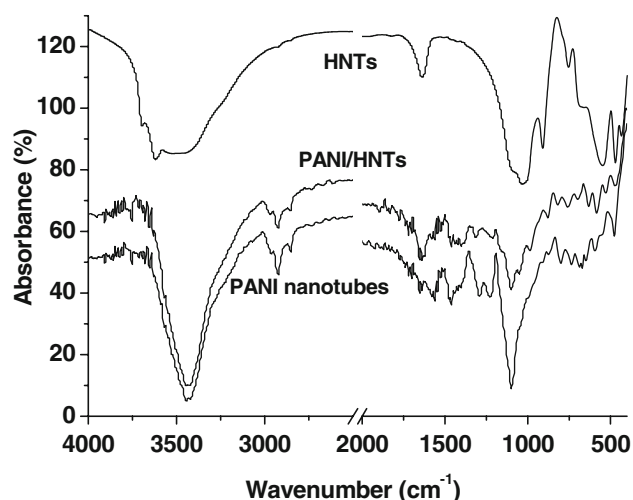


Fig. 3 FT-IR spectra of the HNT templates, PANI/HNTs hybrids, and PANI nanotubes

PANI nanotubes had the inner diameter, outer diameter, and tubular thickness of 40, 60, and 10 nm, respectively.

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